III.A.4 Materials and Process Development Leading to Economical High-Performance Thin-Film Solid Oxide Fuel Cells

Nguyen Minh (Primary Contact), Jie Guan
GE Hybrid Power Generation Systems
19310 Pacific Gateway Drive
Torrance, CA 90502-1031
Phone: (310) 538-7250; Fax: (310) 538-7250; E-mail: nguyen.minh@ps.ge.com

DOE Project Manager: Lane Wilson
Phone: (304) 285-1336; E-mail: Lane.Wilson@netl.doe.gov

Objectives

- Develop a fabrication process for anode-supported solid oxide fuel cells (SOFCs) based on lanthanum gallate electrolytes.
- Identify and evaluate high-performance cathodes for gallate-based SOFCs.
- Demonstrate a gallate-based SOFC that is capable of achieving high performance at reduced temperatures (550 to 800°C).

Approach

- Develop the tape-calendering process to fabricate lanthanum gallate electrolytes.
- Screen cathode materials using cells with self-supported lanthanum gallate electrolytes.
- Modify electrode microstructures and processing parameters to improve electrochemical performance of selected cathode materials.
- Fabricate and characterize thin gallate electrolyte/nickel anode bilayers (also referred to as anode-supported thin gallate electrolyte structures).
- Optimize fabrication process parameters to improve bilayer quality, especially density of the gallate electrolyte.
- Integrate cathodes with thin gallate electrolyte/anode bilayers into single cells and evaluate cell performance at reduced temperatures.
- Analyze cell performance losses and project performance capability.

Accomplishments

- Thin gallate electrolyte structures were fabricated using a tape-calendering process. Fabrication parameters such as raw materials characteristics, tape formulations, and sintering conditions were evaluated. Dense gallate electrolytes with thickness in the range of 10-50 microns were obtained. Use of ceria interlayers with thickness of 3~10 microns between gallate electrolytes and Ni-containing anodes was implemented in the fabrication process.
- Raw material characteristics were found to be critical in the fabrication of thin gallate layers. With high-surface-area lanthanum gallate materials, densification of the thin electrolyte was achieved at sintering temperature of 1350°C.
- Interaction between Ni in anode and lanthanum gallate electrolyte was observed during bilayer fabrication. Decreasing the sintering temperature and increasing the thickness of the ceria barrier layer reduced the migration of Ni from the anode to the gallate electrolyte.

- A high-performance cathode based on $Sr_{0.5}Sm_{0.5}CoO_3$ (SSC) was developed. Performance in the temperature range of 600~800°C was characterized. Low electrode polarization of ~0.23 ohm-cm^2 was achieved at 600°C.
- Performance of thin gallate electrolyte/anode bilayers integrated with high-performance cathodes was characterized. Tested cells generally showed poor performance because of low cell open circuit voltages (OCVs) and interactions between NiO of the anode and the thin gallate electrolyte during fabrication.
- Analysis of performance losses in tested single cells indicated the potential of high cell power densities (up to 1 W/cm^2) at 600°C.

Future Directions

- This project was completed in December 2003. No additional work is planned.

Introduction

The program goal is to advance materials and processes that can be used to produce economical, high-performance solid oxide fuel cells (SOFCs). The overall objective is to demonstrate an SOFC that is capable of achieving extraordinarily high power densities at reduced temperatures. An integrated approach to develop a high-performance, reduced-temperature SOFC is based on the development of materials and structures that result in superior electrolyte and electrode properties. These properties, when combined, are capable of increased performance in the 550 to 800°C temperature range while maintaining function integrity up to 1000°C for short periods.

Approach

The approach is to focus on developing high-performance electrolyte and cathode structures and integrating these structures as thin layers in an anode-supported cell for reduced-temperature (550 to 800°C) operation. The high-performance electrolyte in this project is based on high-conductivity lanthanum gallate [1]. The fabrication of anode-supported thin gallate electrolyte cells is based on the tape-calendering process.

The anode-supported thin electrolyte structure consists of a thin electrolyte (10-50 micron) made of $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.15}Fe_{0.05}O_3$ (LSGMF) or $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_3$ (LSGM). Under the gallate electrolyte is a thin interlayer of ceria that is incorporated to prevent the possible reaction between electrolyte and NiO in the anode. The electrolyte and interlayer are supported by an anode structure consisting of a thin active anode and a thick support anode, both made of Ni-ceria cermet. To improve the quality of the bilayer, efforts are focused on starting material modification and layer structure engineering as well as sintering temperature optimization. Approaches for developing high-performance cathodes include assessing new electrode materials, engineering microstructures, and modifying processing parameters.

Results

Project results are summarized in this section. During the initial development work, fabrication feasibility was explored with available lanthanum gallate powders. It was found that the anode-supported thin gallate electrolyte structure could be fabricated using the tape-calendering process by modifying tape formulations. However, electrolyte densification could only be achieved at higher temperatures (>1450°C). Analysis of the cell microstructure revealed that the electrolyte layer made of coarse gallate materials (surface area ~0.6 m^2/g) contained large grain size and undesired porosity. A considerable amount of Ni was also found in the electrolyte even though a ceria interlayer was used between the electrolyte and the Ni-ceria anode. Similar results on Ni migration were also reported in the literature [2].

To address these issues, several variables such as raw material characteristics, thickness of gallate electrolyte and ceria interlayer, and sintering temperatures were investigated to improve electrolyte densification and reduce Ni migration. For instance, to reduce Ni migration during the fabrication process, ceria barrier thickness was

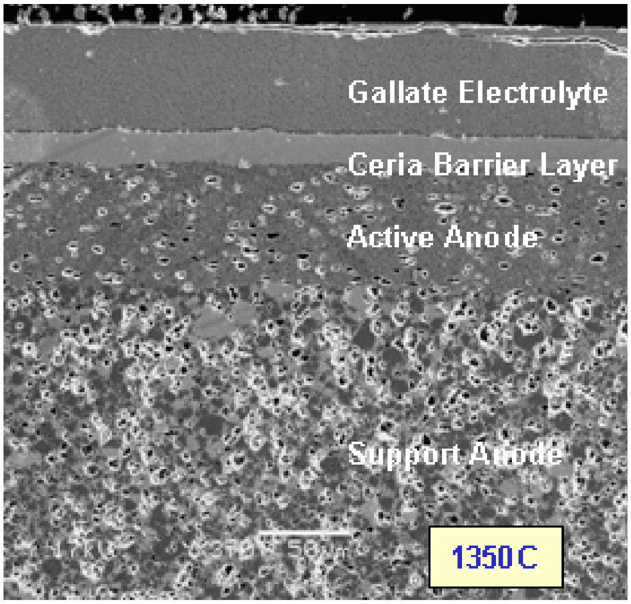

Figure 1. Anode-Supported Thin Gallate Electrolyte Structure Fabricated with Tape-Calendering Process

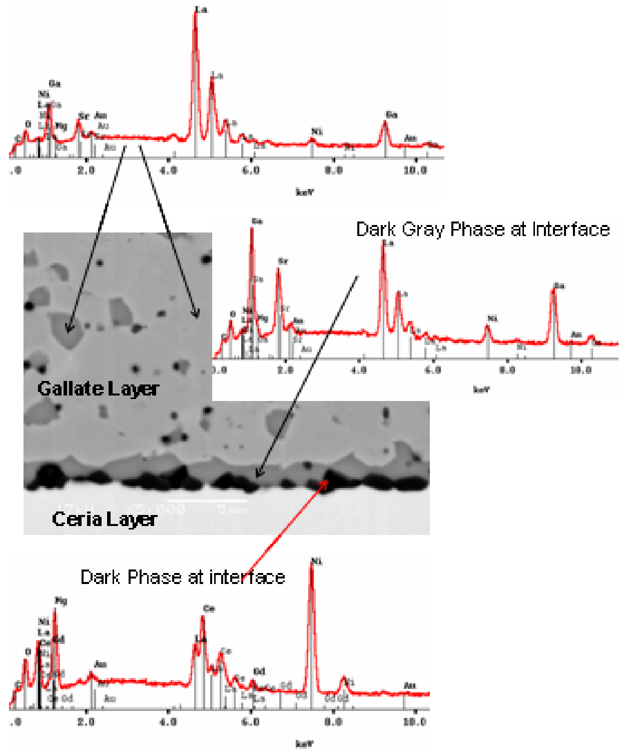

Figure 2. Composition Analysis Showing Ni Migration and Interaction with Gallate Electrolyte

increased to about 8~10 microns and sintering temperature was reduced to 1350°C. The LSGMF electrolyte thickness was also increased to about 50 microns to minimize the possible defects such as pinholes and micro-cracks. As shown in Figure 1, the fabricated bilayer shows dense and continuous structure of ceria barrier layers and gallate electrolytes. Examination of the electrolyte surface and cross-section did not detect significant defects such as pinholes and micro-cracks.

However, in a close examination of polished cross-sections of the fabricated bilayer, Ni-containing phase was reduced but still noticeable (Figure 2), especially at the gallate/ceria interface, even though the ceria interlayer (~10 micron) appeared to be dense and continuous. It is interesting to note that Ni-containing phase was not observed inside the ceria layer except at the interface between gallate electrolyte and the ceria interlayer.

The cathode compositions were selected based on catalytic activity, conductivity, stability, and compatibility with electrolyte at both processing and operating temperatures. Based on the performance screening tests with samarium strontium cobaltite ($Sm_xSr_{1-x}CoO_3$) and lanthanum strontium ferrite (La-Sr-Co/Fe-O_3) materials, the cathode development and evaluation efforts were focused on $Sr_{0.5}Sm_{0.5}CoO_3$ (SSC).

To improve the SSC cathode performance, SSC powder characteristics and processing parameters such as temperature, thickness, and ink solid loading (for screen printing of cathodes on bilayers) were optimized. Cathodic polarizations were reduced to ~0.23 ohm-cm^2 at 600°C with a processing temperature of 1000°C.

In most of the tested cells, the OCVs under N_2/air were about 80-120 mV, indicating good gas tightness of the electrolyte. However, under H_2/air, the OCVs were less than 850 mV compared to the theoretical value of ~1100 mV. The exact causes of the low cell OCVs remain unclear. One hypothesis is that the electrolyte (due to interaction among ceria, NiO and LSGMF) might become mixed conductive under reducing atmospheres. Another hypothesis is that the test cell might crack upon reduction due to its low mechanical strength.

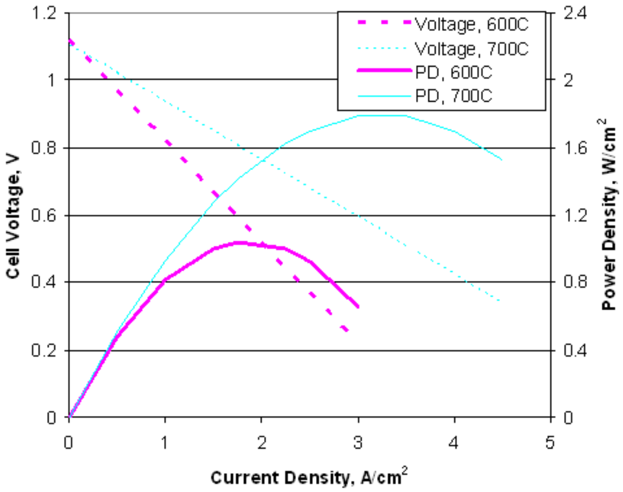

Figure 3. Projected Performance of Anode-Supported 10-micron LSGMF Cells with the Following Conditions: SSC cathode ASR: 0.23 ohm-cm^2 at 600°C, 0.1 ohm-cm^2 at 700°C; Conductivity of LSGMF Electrolyte: 0.024 S/cm at 600°C, 0.072 S/cm at 700°C; Anode ASR: 0.07 ohm-cm^2 at 600°C and 700°C; Air as Oxidant, Hydrogen (2% Humidification) as Fuel

Given the high performance of the SSC cathode and low resistance of highly conductive thin-LSGMF electrolytes, integration of the cathode and the anode-supported thin-LSGMF electrolyte structure is expected to give high cell performance at reduced temperatures if the issues of materials interaction and low mechanical strength can be resolved. Shown in Figure 3 is the projected performance at 600°C and 700°C of a cell with the SSC cathode, 10-micron LSGMF electrolyte, and an anode with polarization equivalent to that of YSZ/Ni anodes for yttria-stabilized zirconia (YSZ) electrolytes. As can be seen, a power density of 1 W/cm^2 should be feasible if the issues relating to thin gallate structure fabrication can be resolved.

Conclusions

Characteristics of lanthanum gallate materials suitable for thin electrolyte structure fabrication were defined in this project. Bilayers with thin and dense lanthanum gallate electrolyte supported on a nickel/ceria anode were successfully fabricated by tape calendering. In the fabrication process, interaction between NiO and lanthanum gallate electrolyte was observed. The interaction was reduced with a ceria interlayer between the electrolyte and the anode. Performance of cathodes based on $Sr_{0.5}Sm_{0.5}CoO_3$ (SSC) was evaluated and improved with material characteristics modification and processing parameters engineering. The improved cathode exhibited excellent performance with cathode polarization of ~0.23 ohm-cm^2 at 600°C. The high-performance SSC cathode and thin gallate electrolyte structures were integrated into single cells, and cell performance was characterized. Tested cells generally showed poor performance because of low cell OCVs. Analysis of cell performance indicated the possibility of achieving high power densities (e.g., 1 W/cm^2 at 600°C) if the issues relating to thin gallate electrolyte fabrication can be resolved.

References

1. T. Ishihara et al., "Nickel-Gd-Doped CeO_2 Cermet Anode for Intermediate Temperature Operating Solid Oxide Fuel Cells Using $LaGaO_3$-Based Perovskite Electrolyte", *Solid State Ionics*, Vol. 132, p. 209, 2000.

2. S. Elangovan et al, "Lanthanum Gallate Electrolyte for Intermediate Temperature Operation", Electrochemical Society Proceeding, Vol. 2003-07, p. 299, 2003.